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**MANIPULATION OF THE WETTABILITY OF SURFACES ON THE 0.1 TO 1
MICROMETER SCALE THROUGH MICROMACHINING AND MOLECULAR
SELF-ASSEMBLY**

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Through Micromachining and Molecular Self-Assembly

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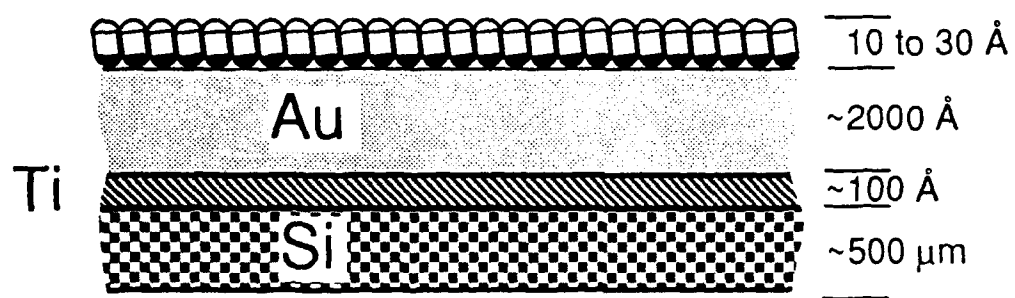
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Micromachining allows the formation of micrometer-sized regions of bare gold on the surface of a gold film supporting a self-assembled monolayer (SAM) of alkanethiolate. A second SAM forms on the micromachined surfaces on exposing the entire system -- the remaining undisturbed gold-supported SAM and the micromachined features of bare gold -- to a solution of dialkyldisulfide. By preparing an initial hydrophilic SAM from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$, micromachining features into this SAM, and covering these features with a hydrophobic SAM formed from $[\text{CH}_3(\text{CH}_2)_{11}\text{S}]_2$, it is possible to construct micrometer-scale hydrophobic lines in a hydrophilic surface. These lines provide new structures with which to manipulate the shapes of liquid drops.

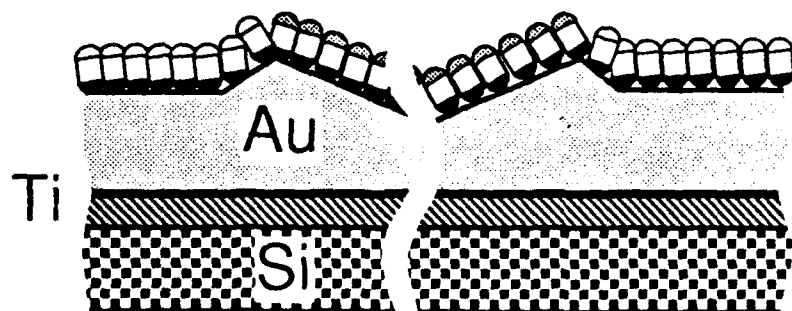
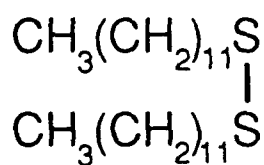
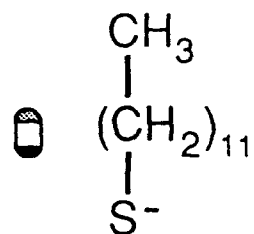
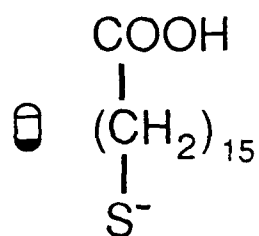
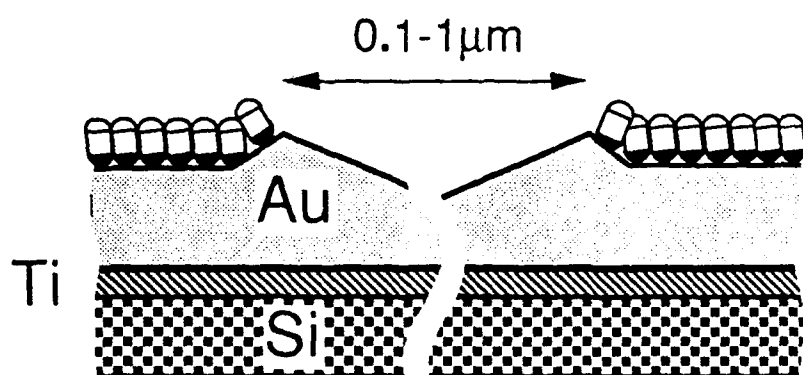
A combination of micromachining (1) and molecular self-assembly provides the basis for a new procedure to generate micrometer-scale patterns of contrasting surface properties. This procedure has three steps: (i) formation of an initial self-assembled monolayer (SAM) of alkanethiolate on gold (2); (ii) generation of regions of bare gold in the SAM by micromachining; and (iii) formation of a second SAM on these micromachined regions. Because the two SAMs can have different compositions and physical properties, and because the shapes of the micromachined features (3) can be controlled, this process controls the characteristics of a surface with micrometer resolution without the use of photolithography. We illustrate the capability of this new type of microfabrication by forming patterns of SAMs of contrasting wettability on gold surfaces and by using these patterns to manipulate the shapes of drops of water.

The experimental procedure is summarized in Fig. 1. First, a hydrophilic SAM was formed by reaction of a gold film (4) with ω -mercaptohexadecanoic acid ($\text{HS}(\text{CH}_2)_{15}\text{COOH}$) (5). The carboxylic acid group makes the surface hydrophilic, with wettability dependent on the pH of the water: the contact angle [measured under cyclooctane(5)] decreased from $\theta_a^{\text{H}_2\text{O}} = 30^\circ$ (pH 5) to $<5^\circ$ (pH 10). Second, 0.1 to 1 μm -

Fig. 1. Schematic illustration of the formation of 0.1 to 1 μm scale hydrophobic lines in a hydrophilic surface with micromachining and SAMs. We imply no asymmetry in the structure of the SAMs within the micromachined groove. Au = evaporated film of gold; Ti = evaporated film of Ti used to promote adhesion of the Au to the silicon wafer (Si).



micromachine



scale features of bare gold were micromachined into the surface of the gold supporting the SAM. Either a surgical scalpel blade or the cut end of a carbon fiber was used as a tool (6). We used a 3 mN load on the tip of the scalpel to machine uniform grooves with macroscopic lengths (≥ 1 cm), widths of ~ 1 μm , and depths of ~ 0.05 μm (Fig.2). The micromachined grooves were bordered by two lips of raised metal (~ 0.1 μm high and ~ 0.2 μm wide) formed by the plastic deformation of the gold during machining (7). Each lip presents an inclined surface to the edge of a spreading drop of liquid and influences the wetting behavior of the surface. In contrast, much smaller lips of metal bordered the ~ 0.1 μm -wide grooves that were formed with the tip of a carbon fiber (8). Third, a second, hydrophobic SAM was formed selectively on the bare gold features by immersing the micromachined surface in a solution of $[\text{CH}_3(\text{CH}_2)_{11}\text{S}]_2$. We used a dialkyldisulfide in this step because dialkyldisulfides replace surface thiolates in SAMs approximately 10^2 more slowly than do the corresponding alkanethiols, and thus minimize the modification of the properties of the original hydrophilic SAM while forming the second hydrophobic SAM (9,10).

Features on the 0.1 to 1 μm -scale having contrasting wettability can pin the edges of drops of water. The extent of this pinning was influenced by the type of SAM within the micromachined groove and by the shape of the groove (11). We have used 0.1 to 1 μm wide grooves having hydrophobic SAMs to manipulate the positions and the shapes of drops: several features that can be controlled are illustrated in Fig. 3. Drops can be positioned with edges straight and pinned close together: the resolution of a side view of two drops with edges pinned by a common, 1 μm -wide line is limited by the effects of diffraction and reflection, but the drop edges are clearly separated by less than 30 μm (12). The drops do not appear to communicate with one another: a dye in one compartment remains localized and does not diffuse into neighboring compartments. The extent of wetting of the corners of the pattern depends on the contact angle of the water on the SAM (and thus, in this system, on the pH of the

Fig. 2. Scanning electron micrographs of the scalpel (A and B) and the carbon fiber (D and E). The inset in A is a low magnification image (x10 magnification) of the tip of the scalpel. The grooves C and F (marked by an arrow) were micromachined into a gold film bearing a SAM formed from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$. The samples were fractured normal to the groove in liquid nitrogen for imaging. The sizes and shapes of the grooves are probably determined by local features of the tip of the scalpel and fiber.

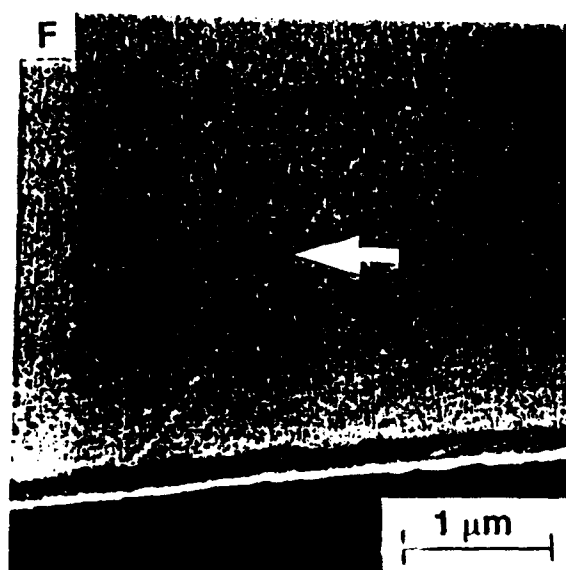
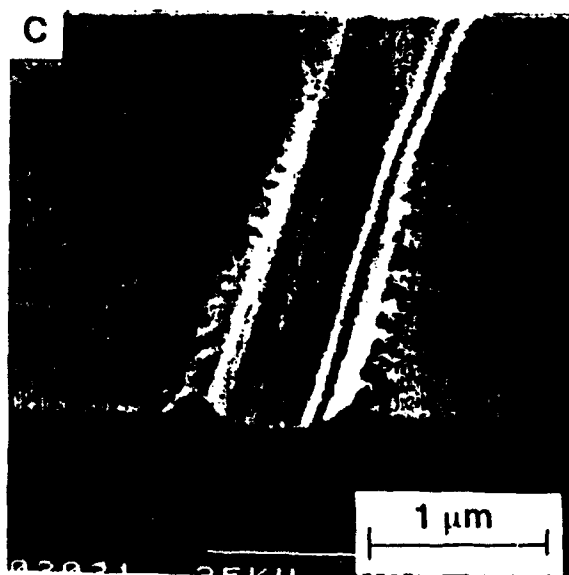
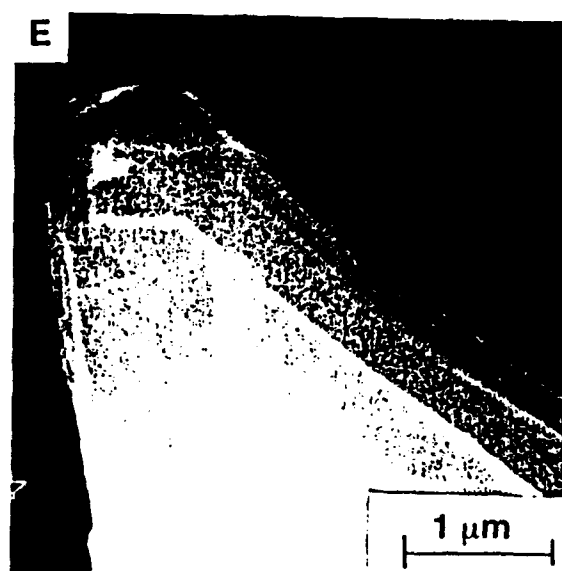
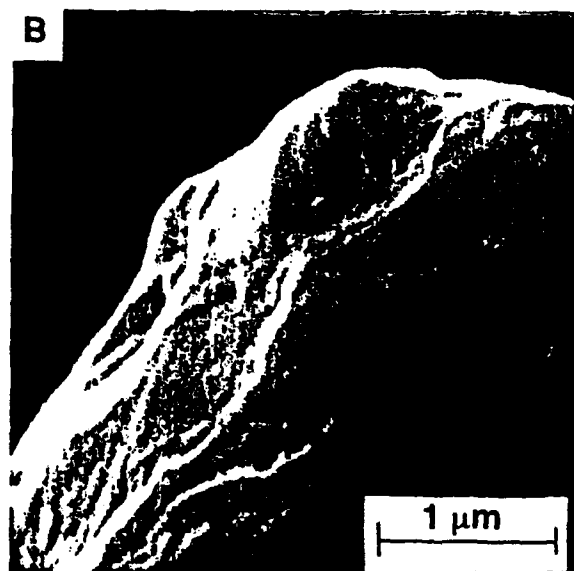
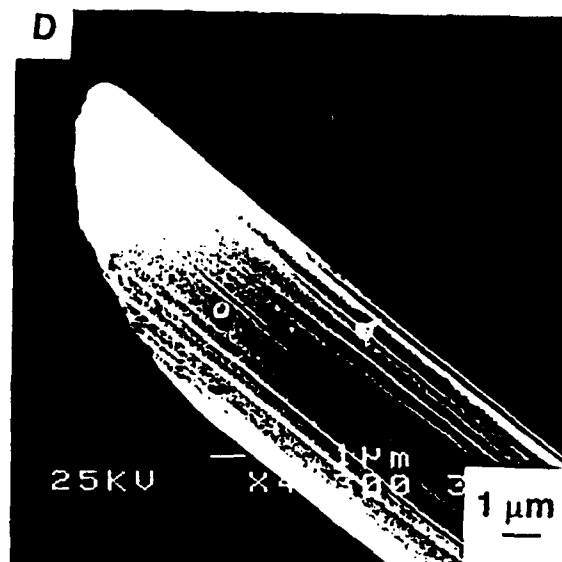
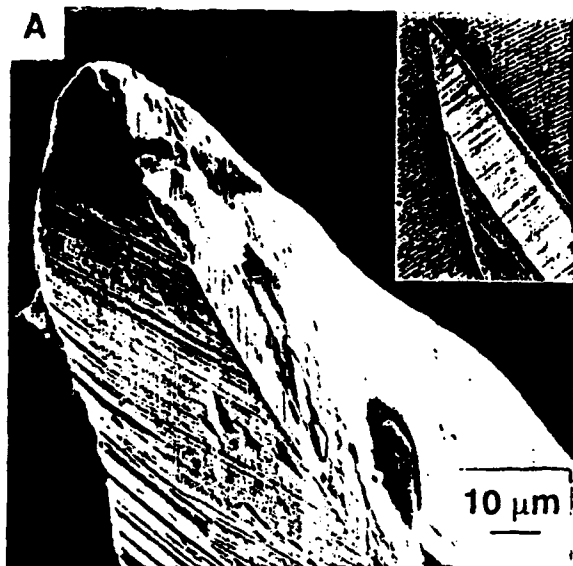
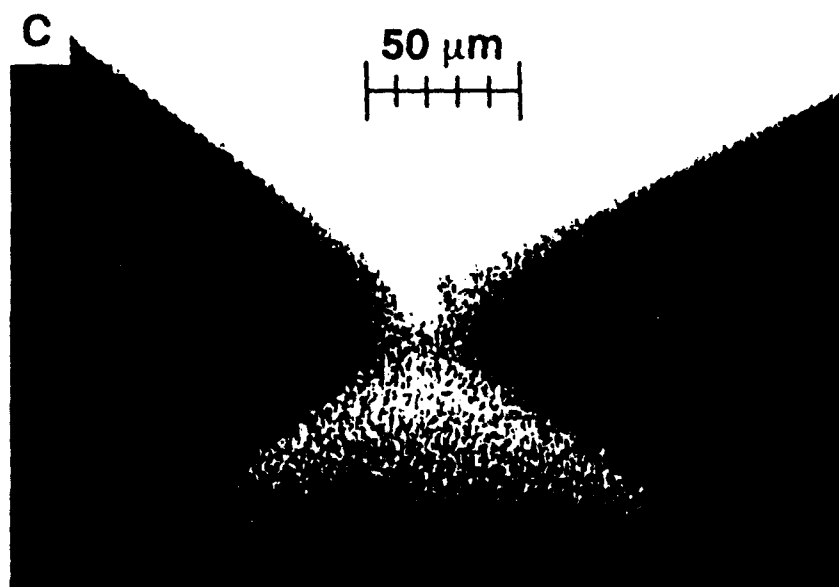
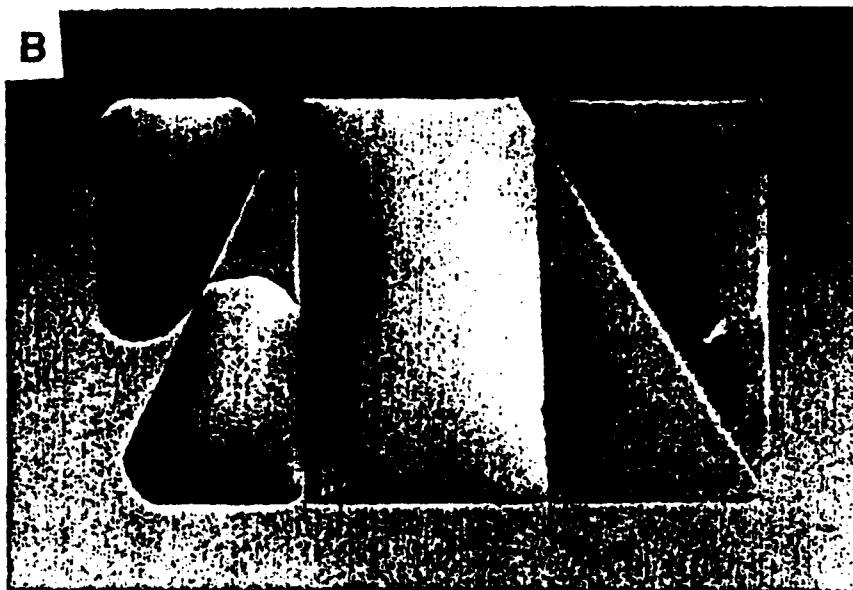
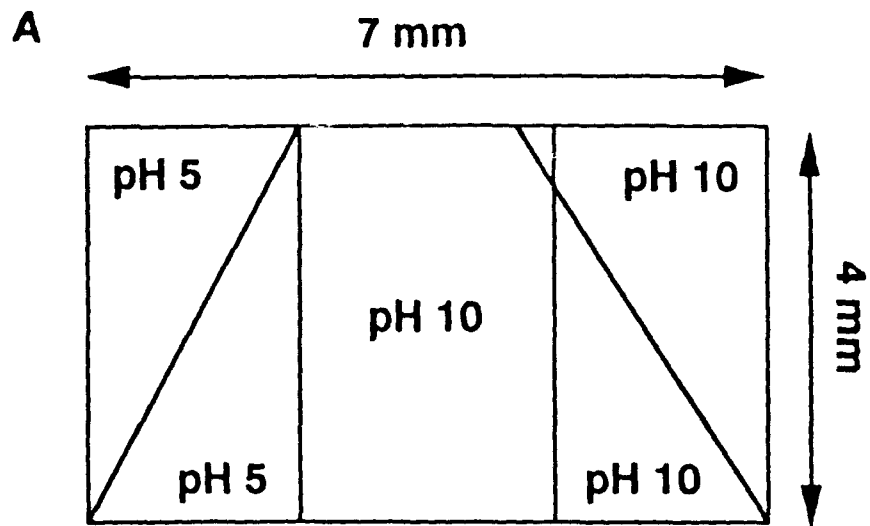


Fig. 3. Top and sides views of drops of water on a SAM formed from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ and patterned with micrometer-scale micromachined grooves [see Fig. 2(c)] supporting a SAM formed from $[\text{CH}_3(\text{CH}_2)_{11}\text{S}]_2$: (A), diagram of grooves; (B), top view of drops; (C), side view of two drops separated by hydrophobic groove. The pH values of the buffered drops of water are shown in (A). Note also that the hydrophobic line that forms the hypotenuse of the triangular drops of pH 10 water cuts off the top right corner of the rectangular drop; a dust particle can be seen on a triangular pH 10 drop; and the circular edge of a pH 5 drop is slightly pinned. The dark regions in (C) are the two water drops which almost meet at the hydrophobic line in the center of the photograph. The top surface of each dark region is the air-water interface and the apparent bottom surface is caused by the reflection and diffraction of light in the vicinity of the closely positioned edges of the two drops.



water), the angle at the corner, and the volume of liquid in the drop.

Control experiments in which the initial SAM and the second SAM deposited on the surface of the micromachined features were both formed from $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ showed little or no pinning of a drop (pH 10, 0.05M borate) (11). Micromachined features with hydrophobic SAMs having 0.1 μm widths showed a weaker tendency to pin a drop than those with 1 μm widths. We have not quantified the importance of the width of the groove and the shape of its edge in pinning the edge of the drop (13,14).

The combination of micromachining with molecular self-assembly offers a versatile new procedure for manipulating the structure and properties of surfaces, and the shapes of liquids drops on them. Micromachining provides both convenient access to small features and control over the geometry of these features. By using simple procedures we have generated features that are already smaller (0.1 μm) than those that can be routinely generated with optical lithography (15). With the use of improved micromachining tools (including the scanning tunneling microscope), it should be possible to extend this technique to create features with sizes of 10 nm or smaller. Molecular self-assembly is particularly useful as a part of this procedure because it allows molecules to be adsorbed on very small features (<1nm) with high selectivity and because it permits sensitive control of the surface free energies (16).

The procedure illustrated in Fig. 3 is an uncomplicated one that uses a gold support, one width for the grooves, and two different SAMs. The procedure can be extended to other supports and geometries of the grooves and, through combinations of sequential pattern formation and orthogonal self-assembly (17), to multiple combinations of SAMs. We believe that this procedure can be readily generalized and widely useful in controlled patterning of surfaces. It provides an alternative to optical lithography, and should be applicable to problems where optical techniques are not (such as, nonplanar substrates) and in laboratories where optical lithography is not

available. The ability to manipulate the shapes of drops should be applicable to problems in wetting and adhesion, and to the characterization of surfaces (18).

References and Notes

1. We use the term micromachining to mean the moving of metal by a mechanical means rather than chemical etching.
2. R.G. Nuzzo and D.L. Allara, *J. Am. Chem. Soc.* **105**, 4481 (1983); C.D. Bain and G.M. Whitesides, *Angew. Chem. Int. Ed. Engl.* **101**, 522 (1989), and references therein; G.M. Whitesides and P.E. Laibinis, *Langmuir* **6**, 87 (1990), and references therein.
3. We use the term feature to mean a region of the surface with a property that is distinguishable from its surroundings.
4. The gold substrates were prepared by evaporation of 100 Å of Ti (99.999%) onto a polished silicon(100) wafer (Silicon Sense, Nashua, New Hampshire) followed by 2000 Å of Au (99.999%) with an electron beam evaporator operating at a pressure of less than 10^{-6} torr.
5. C.D. Bain and G.M. Whitesides, *Langmuir* **5**, 1370 (1989); S.R. Holmes-Farley, C.D. Bain, G.M. Whitesides, *ibid* **4**, 921 (1988).
6. The depth and width of the micromachined grooves could be controlled by varying the load (1.2 to 9.8 mN) on the tip of the scalpel blade (Feather Industries, Tokyo, Japan) and carbon fiber (diameter 8 μm). By using energy dispersive x-ray fluorescence measurements we detected no evidence of exposed silicon within the micromachined groove.
7. The plastic deformation of the gold suggests the machining pressure exceeded the yield strength of the gold. Assuming a scapel tip area of $10\ \mu\text{m}^2$ in contact with the gold surface, a load of 3 mN corresponds to a tip pressure of 30 MPa. This pressure is comparable to the yield strength of bulk gold (3.4 to 14 MPa, -depending on thermal

history) and the ultimate tensile strength of bulk gold (131 MPa) [E.M. Wise, *Gold; Recovery, Properties and Application*, (Van Nostrand, New York, 1964)].

8. Scanning electron microscopy images of the tip of the carbon fiber showed a morphology resembling thin parallel sheets. These tips sometimes formed distinct parallel grooves, separated by as little as $0.1\mu\text{m}$.

9. By using a dialkyldisulphide to form the second SAM, the exchange with thiolates of the first SAM can be reduced to less than 0.1%. For example, a SAM formed from $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$ has been measured, by using the contact angles of water on the SAM and x-ray photoelectron spectroscopy, to exchange less than 0.1% when exposed to a 0.1 mM solution of $[\text{HO}(\text{CH}_2)_{11}\text{S}]_2$ in ethanol for 10 s at 25°C [H.A. Biebuyck and G.M. Whitesides, unpublished results].

10. We have also formed the second SAM using a 0.1 mM solution of $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{SH}$ in ethanol and very short (~ 1 s) adsorption times. The rate of reaction of $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{SH}$ with the bare gold is faster by a factor of 10 than the rate of its exchange into the first SAM [C.D. Bain, E.B. Troughton, Y.-T. Tao, J. Evall, G.M. Whitesides, R.G. Nuzzo, *J. Am. Chem. Soc.* **111**, 321 (1989); C.E.D. Chidsey, C.R. Bertozzi, T.M. Putvinski, A.M. Muzsice, *ibid.* **112**, 4301 (1990); D.M. Collard, M.A. Fox, *Langmuir*, **7**, 1192 (1991); C.D. Bain, H.A. Biebuyck, G.M. Whitesides, *ibid.* **5**, 723 (1989)].

11. Although grooves formed with a load of 3 mN applied to the tip of the scalpel did not pin the edges of drops, grooves formed with larger loads (≥ 10 mN) showed a weak tendency to pin drops. Because larger loads produce larger grooves, this suggests that the shapes of the grooves can influence the pinning of drops.

12. Top views of the drops under an optical microscope indicated the separation of the drops was $\leq 5\mu\text{m}$.

13. These observations are consistent with the established influence of "surface roughness" (including grooves) on the wetting of solid surfaces with liquids [P.G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985), and references therein].
14. Drops of water can also be pinned by "writing" lines of SAMs with liquid alkanethiols. In this case there is no deformation of the surface. [H.A. Biebuyck and G.M. Whitesides, unpublished].
15. We use the term optical lithography to mean lithography with radiation wavelengths in the range 248 nm (KrF excimer laser) to 436 nm (mercury arc source) [J. Bruning, *Opt. Photonics News*, May, 23 (1991)].
16. The rate of lateral diffusion of molecules in the SAM is unknown but may ultimately limit the resolution of the method.
17. P.E. Laibinis, J.J. Hickman, M.S. Wrighton, G.M. Whitesides, *Science* **245**, 845 (1989).
18. The analysis of wetting in the corners can yield fundamental information such as the contact angle of the liquids on the SAMs.
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